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COMPLETE SPECIFICATION

Colour Photographic Development employing Pyrazolones as Colour Couplers

We, EASTMAN KODAK COMPANY, a Company organized under the Laws of the State of New Jersey, United States of America, of 343, State Street, Rochester, New York 14650, United States of America, (Assignee of DAVID VALENTINE YOUNG), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to colour photographic development employing pyrazolones as colour couplers. In particular, it relates to a process of colour development, to photographic emulsions containing colour couplers, to photographic elements and to colour couplers themselves.

Formation of coloured photographic images in photographic development by the coupling of the oxidation products of aromatic primary amino developing agents formed during photographic development of silver halide emulsions with colour couplers is well known. In the subtractive process of colour photography the image dyes formed from the colour couplers are of the complementary colours cyan, magenta and yellow. The colour couplers used to produce the cyan dyes are usually phenols or naphthols; those used to produce the magenta dyes are usually pyrazolones or cyanoacetyl compounds; and those used to form the yellow dyes are usually open-chain compounds containing a methylene group having one or two carbonyl groups attached to it. In photographic elements for three-colour photography wherein the couplers are incorporated in the emulsions, the cyan-forming couplers are usually in the red-sensitive emulsion, the magenta-forming couplers are usually in the green-sensitive emulsion and the yellow-forming couplers are usually in the blue-sensitive emulsion. Sometimes the couplers are incorporated in the colour developing baths.

Colour couplers whose solubility or dispersibility is sufficient to enable them to be usefully incorporated in aqueous colour developing baths are referred to as "diffusible-type couplers". Colour couplers of such high molecular weight and/or complex molecular structure that they are capable of remaining during colour development, in photographic hydrophilic colloid-silver halide emulsion

layers in which they have been incorporated are referred to as "non-diffusing couplers". Non-diffusing couplers having carboxylic or sulphonic groups rendering them soluble in aqueous alkali are referred to as "Fischer-type couplers". Non-diffusing couplers having no such solubilizing groups are somewhat hydrophobic and are generally incorporated in hydrophilic colloid-silver halide emulsions with the aid of high-boiling solvents.

When the dye image formed on colour development is to be used *in situ*, e.g. as, or as part of, a colour transparency or colour print, the coupler must be one which gives a substantially non-diffusing dye. The dye image used for image transfer processes should be diffusible but capable of being mordanted or fixed in the receiving sheet. For this purpose a coupler is selected which will produce this type of dye.

Colour couplers have a reactive group, usually a reactive methylene group, which reacts with the oxidation products of the primary aromatic amino developing agent producing azo-methines, indamines or indophenols depending upon the nature of the colour coupler and of the developing agent. If the reactive group is an unsubstituted reactive methylene group, then for the formation of each equivalent of dye there are required the oxidation products resulting from the development of 4 equivalents of silver. This will be apparent from the formulae given for the coupling reaction on pages 390 to 393 of "The Theory of the Photographic Process" by C. E. K. Mees, The McMillan Co., New York, (Edited by T. H. James), 1966. These couplers can therefore be referred to as 4-equivalent couplers.

It is, however, known that if one of the hydrogen atoms of the reactive methylene group is replaced by a halogen atom, such as an atom of chlorine, coupling will still take place with the production of the same dye as is formed when the reactive methylene group is unsubstituted. The halogen atom is displaced in the coupling reaction but the effect of this displacement is that for the production of one equivalent of dye there are required the oxidation products resulting from the production of only 2 equivalents of silver. These couplers are, therefore, referred to as 2-equivalent couplers; see, for example, Specification No. 736,922.

2-Equivalent couplers have some important advantages over 4-equivalent couplers. Since they require for the production of the coupled dye only half the amount of silver halide which is required in the case of 4-equivalent couplers, there is a reduction in the cost of making the emulsions and also an improvement in the quality of the images produced. The reduction in quantity of silver halide required with 2-equivalent couplers makes it possible to use thinner emulsion layers and it is known that reducing the thickness of emulsion layers results in improved image definition and resolution. Moreover, reduction of emulsion thickness has the further advantage of decreasing the opacity of the emulsion allowing more light to penetrate into an underlying emulsion layer. The use of 2-equivalent couplers, therefore, gives useful advantages in the production of coloured images in multilayer materials. Thin image-forming layers are very desirable because they cause less light scattering and produce sharper images.

Certain of the available 2-equivalent couplers exhibit serious disadvantages such as low reactivity, formation of an unacceptably high level of colour fog, and other undesirable side reactions.

The couplers of the present invention have a materially reduced tendency to produce unwanted colour density in the non-image areas. They also have a greatly reduced propensity to unwanted side reactions and hence give a higher dye yield. They also have greatly increased reactivity, thereby obviating prolonged or forced development.

The invention also provides a simple, economical and reproducible process for preparing the colour couplers in high yield.

It has now been found that 2-equivalent couplers result when one of the hydrogen atoms of the active methylene group in a pyrazolone nucleus is replaced with an aryloxy or substituted aryloxy radical, e.g., oxyaryloxy or arylenedioxy.

According to one feature of the present invention, there is provided a colour coupler containing at least one 4-pyrazolyl-5-one group having attached to the carbon atom in the 4-position, a hydrogen atom and an aryloxy or substituted aryloxy group. This aryloxy or substituted aryloxy group is split off during coupling development.

The couplers of the invention may be represented by the formula:

$$\text{I} \qquad \left[\text{RO}-\right]_{n}\text{R}^{1}$$

wherein n represents 1 or 2,

R represents a 4-pyrazolyl-5-one group, and

R^1 represents an aryl group when n represents 1 or an arylene group when n represents 2.

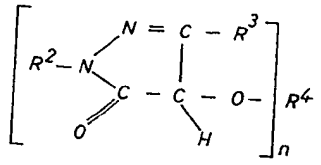
Many pyrazol-5-ones are described in the literature and have been used as colour couplers in colour photography. It is known that coupling takes place in the 4-position of the nucleus.

Although the effectiveness of the couplers of the invention as 2-equivalent couplers is not dependent on the specific composition of R and R^1, it will be understood that these radicals may contain various substituent groups and that the character and the degree of sub-

stitution may be modified according to such requirements, e.g., spectral absorbtivity, reactivity, solubility, and diffusibility, as may be imposed by the photographic system in which the coupler is to be used.

The preferred colour couplers are those, represented by the general formula:

(III)



wherein R^2 represents an alkyl group, a monocyclic alkyl group, a bicyclic alkyl group, a substituted alkyl group, an aryl or substituted aryl group, a heterocyclic group (substituted or unsubstituted), a carbamyl group or a thiocarbamyl group,

R^3 represents a hydrogen atom, an alkyl or substituted alkyl group, an aryl or substituted aryl group, a heterocyclic group (unsubstituted or substituted), a carboxy ester group, an etherified hydroxyl group, an etherified thiol group, an amino or substituted amino group, an acylamino group, a carbamyl group, a sulphamyl group, a ureido group, a thioureido group or a guanidino group,

n represents 1 or 2,

R^4 represents an aryl or substituted aryl group when n represents 1, or an arylene or substituted arylene group when n represents 2.

The alkyl group represented by R^2 may be a straight or branched chain alkyl group having from about 1 to 30 carbon atoms, preferably from 1 to 22 carbon atoms (e.g., methyl, isopropyl, tertiary butyl, hexyl, dodecyl or docosyl).

If the group represented by R^2 is a bicyclic alkyl group this may be, for example, a terpenyl group especially a norbornyl group (e.g., norbornyl, 7,7-dialkylnorbornyl, 2-phenyl-7,7-dialkylnorbornyl or 2-pentadecyl-7,7-dialkylnorbornyl).

If the group represented by R^2 is a substituted alkyl group, the substituent or substituents may be any of the substituent groups used in colour couplers, such as a halogen atom, the nitro group, the hydroxyl group, the carboxyl group, an amino or substituted amino group (e.g., amino, N-alkylamino, N,N-dialkylamino, N-arylamino, N-alkyl or N-arylamino), a carboxy ester group (e.g., carbomethoxy, carboethoxy or carbophenoxy), the sulpho group, a sulpho ester group (e.g., methoxysulphonyl, butoxysulphonyl or phenoxysulphonyl), an amido group (e.g., acetamido, butyramido, [α - (2,4 - di - t-amylphenoxy)acetamido]benzamido, α - (3-pentadecylphenoxy)butyramido, α - (4 - t-butylphenoxy)propionamido, 3,5 - dicarboxybenzamido, ethylsulphonamido or phenylsulphonamido), a carbamyl group (e.g., N-methylcarbamyl or N-phenylcarbamyl), a sulphamyl group (e.g., N-propylsulphamyl or N-tolylsulphamyl), an alkoxy group (e.g., methoxy or butoxy), an aryloxy group (e.g., phenoxy, tolyloxy or naphthoxy).

If the group represented by R^2 is a heterocyclic group this may be one having from 5 to 6 atoms in the ring including nitrogen, sulphur or oxygen as the heteroatoms, for example furanyl, benzothiazolyl, oxazolyl, imidazoyl or quinolinyl. If it is a substituted heterocyclic group the substituents may be any of those described above as substituents for alkyl groups.

If the group represented by R^2 is a carbamyl or thiocarbamyl group this may be alkylcarbamyl, alkylthiocarbamyl, arylcarbamyl, arylthiocarbamyl, heterocyclcarbamyl or heterocycylthiocarbamyl, in which the alkyl, aryl or heterocyclic groups may be substituted with any of the substituents described above as substituents for alkyl groups.

If the group represented by R^3 is a substituted alkyl, aryl or heterocyclic group, the substituents may be any of those described above as substituents for alkyl groups represented by R^2.

Examples of the other groups which R^3 may represent are carbopropoxy, carbobutoxy, carbophenoxy, methoxy, ethoxy, decycloxy, phenoxy, tolyloxy, ethylthio, propylthio, phenylthio, tolylthio, N-alkylamino, N-arylamino, N,N-dialkylamino, N-alkyl, N-arylamino, acetamido, α - (2,4 - di - t - amylphenoxy)acetamido, α - butylphenoxypropionamido, α - (3 - pentadecyl - 4 - sulphophenoxyacetamido)benzamido, carbamyl, N-octadecylcarbamyl, N,N - di - hexylcarbamyl, N - methyl - N - phenylcarbamyl, 3 - pentadecylphenylcarbamyl, ureido, N - arylureido, N - alkylureido, N - alkylthioureido, N-arylthioureido, guanidino, N-arylguanidino or N-alkylguanidino.

The alkyl and aryl groups in R^3 may contain as substituent groups any of those described above as substituents for alkyl groups represented by R^2.

Examples of aryl and substituted aryl groups which R^4 may represent are phenyl, alkylsulphonylphenyl, arylsulphonylphenyl, N-alkylsulphamylphenyl, N,N-dialkylsulphamylphenyl, N-arylsulphamylphenyl, N - alkyl-N - arylsulphamylphenyl, sulphamylphenyl, nitrophenyl acetamidophenyl, halophenyl, naphthyl, pyridyl, methoxyphenyl, octadecoxyphenyl, hydroxyphenyl, sulphophenylazophenyl, carboxyphenyl or sulphophenyl.

Examples of arylene and substituted arylene groups which R^4 may represent are phenylene, naphthylene, diphenylene, pyridylene, quinolylene, diphenylene sulphone or ω,ω-

phenylene alkyl. The alkyl and aryl groups in R^1 may contain as substituent groups any of those described above as substituents for alkyl groups represented by R^2.

The aryloxy or substituted aryloxy group on the coupling position of the colour couplers of the present invention gives them good coupling reactivity and other valuable properties. These couplers are particularly characterized by the low levels of unwanted colour fog, printout and yellowing they produce in photographic elements using them for image formation. Excellent coupling reactivity is obtained with the colour couplers of the invention even when incorporated in emulsion layers without the use of high-boiling solvents. When high-boiling solvents are used to disperse these couplers, high dye yield and low colour fog are attained over a wide range of coupler-to-solvent ratios. When the diffusible couplers of the invention are used in colour developing solutions, excellent reactivity and good dye yield are achieved.

The invention further includes an image-forming layer containing a colour coupler which is as defined above.

The invention further includes a light-sensitive hydrophilic colloid silver halide emulsion containing a colour coupler which is as defined above. The hydrophilic colloid is preferably gelatin.

The invention also includes a photographic element comprising a support bearing at least one layer containing a photographic emulsion, as defined above.

The invention further includes a process of colour development which includes developing a reducible silver salt image with a primary aromatic amino developing agent in the presence of a colour coupler which is a compound as defined above.

The 2-equivalent couplers of the present invention may be diffusible-type couplers, Fischer-type couplers or non-diffusible-type couplers. The non-diffusible-type couplers are readily incorporated in light-sensitive hydrophilic colloid-silver halide emulsion layers over a wide range of coupler to solvent ratios. Some of the non-diffusible-type couplers of the present invention have good coupling reactivity even when incorporated in emulsion layers with no high-boiling coupler solvents; these couplers can be advantageously used in thin emulsion layers to produce very sharp images.

The invention further includes a colour developer containing a primary aromatic amino developing agent and a diffusible colour coupler which is as defined above.

The following named colour couplers will serve to illustrate but not limit the invention. Their structural formulae are shown in the correspondingly numbered figures of the accompanying drawings.

Coupler 1. 1-Phenyl-3-methyl-4-(4-methylsulphonylphenoxy)-5-pyrazolone.

Coupler 2. 1-(4-Sulphphenyl)-3-methyl-4-[4-(N-methyl-N-n-octadecylsulphamyl)-phenoxy]-5-pyrazolone sodium salt.

Coupler 3. 1-(2,4,6-Trichlorophenyl)-3-{3-[α-(2,4-di-t-amyl-phenoxy)-acetamido]benzamido}-4-(4-nitrophenoxy)-5-pyrazolone.

Coupler 4. 1-Phenyl-3-methyl-4-(2,4-dinitrophenoxy)-5-pyrazolone.

Coupler 5. 1-Phenyl-3-anilino-4-phenoxy-5-pyrazolone.

Coupler 5. 1-Phenyl-3-n-octadecylamino-4-(4-nitrophenoxy)-5-pyrazolone.

Coupler 7. 1-Phenyl-3-n-octadecylamino-4-(4-acetamidophenoxy)-5-pyrazolone.

Coupler 8. 1-{4-[α-(3-n-Pentadecylphenoxy)-n-butyramido]-phenyl}-3-ethoxy-4-(4-nitrophenoxy)-5-pyrazolone.

Coupler. 9 1-Phenyl-3-pentadecyl-4-(2-chloro-4-sulphamylphenoxy)-5-pyrazolone

Coupler 10. 1-(4-Stearamidophenyl)-3-ethoxy-4-(2,4-dinitrophenoxy)-5-pyrazolone.

Coupler 11. 1-[4-(4-t-Butylphenoxy)phenyl]-3-[α-(4-t-butylphenoxy)-n-propion-amido]-4-(pentafluorophenoxy)-5-pyrazolone.

Coupler 12. 1-[4-(4-t-Butylphenoxy)phenyl]-3-[α-(4-t-butylphenoxy)-n-propion-amido]-4-(1-naphthyloxy)-5-pyrazolone.

Coupler 13. 1-[4-(4-t-Butylphenoxy)phenyl]-3-[α-(4-t-butylphenoxy)-n-propion-amido]-4-(4-pyridyloxy)-5-pyrazolone.

Coupler 14. 1-[4-t-Butylphenoxy)phenyl]-3-[α-(4-t-butylphenoxy)-n-phenoxy)-propionamido]-4-(4-chlorophenoxy)-5-pyrazolone.

Coupler 15. 1-Methyl-3-(3,5-dicarboxybenzamido)-4-(4-nitro-3-n-pentadecyl-phenoxy)-5-pyrazolone.

Coupler 16. 1-Phenyl-3-n-octadecylcarbamyl-4-[4-(N-methyl-N-phenylsulphamyl)-phenoxy]-5-pyrazolone.

Coupler 17. 1-(2,4,6-Trichlorophenyl)-3-{3-[α-(2,4-di-t-amylphenoxy)acet-amido]benzamido}-4-[4-(4-hydroxyphenylsulphonyl)phenoxy]-5-pyrazolone.

Coupler 18. 1-Phenyl-3-(3,5-dicarboxyanilino)-4-(4-n-octadecyloxyphenoxy)-5-pyrazolone.

Coupler 19. 1-Phenyl-3-[N'-(α,{-dicarboxyethyl)ureido]-4-(4-nitro-3-n-penta-decylphenoxy)-5-pyrazolone.

Coupler 20. 1-(2,4-Dichloro-6-methoxyphenyl)-3-{3-[α-(3-n-pentadecyl-4-sulphophenoxy)acetamido]benzamido}-4-(4-nitrophenoxy)-5-pyrazolone.

Coupler 21. 1-(2,4-Dichloro-6-methoxyphenyl)-3-{3-[α-(3-n-pentadecyl-4-sulphophenoxy)acetamido]benzamido}-4-(4-acetamidophenoxy)-5-pyrazolone.

Coupler 22. 1-Phenyl-3-{2-chloro-4-{3-[α-(3-n-pentadecyl-phenoxy)acetamido]-benzamido}anilino}-4-[4-(4-sulphophenylazo)phenoxy]-5-pyrazolone.

Coupler 23. 1-(2,4,6-Trichlorophenyl)-3-{5-[α-(2,4-di-t-amylphenoxy)acetamido]-2-methoxyanilino}-4-[4-(N,N-diethylsulphamyl)phenoxy]-5-pyrazolone.

Coupler 24. 1-{4-[α-(3-t-Butylphenoxy)-n-tetradecanamido]-2,6-dichlorophenyl}-3-(2,4-dichloroanilino)-4-(4-methylsulphonylphenoxy)-5-pyrazolone.

Coupler 25. 1-(2,4,6-Trichlorophenyl)-3-{2-[α-(3-n-pentadecylphenoxy)acet-amido]anilino}-4-(4-nitrophenoxy)-5-pyrazolone.

Coupler 26. 1-(2,4,6-Trichlorophenyl)-3-{2-[α-(3-n-pentadecylphenoxy)acetamido]-anilino}-4-(4-acetamidophenoxy)-5-pyrazolone.

Coupler 27. 1-(2,4,6-Trichlorophenyl)-3-(4-nitroanilino)-4-(4-sulphamylphenoxy)-5-pyrazolone.

Coupler 28. 1-(2,4,6-Trichlorophenyl)-3-{2-chloro-4-[α-(2,4-di-t-amylphenoxy)-n-butyramido]anilino}-4-(4-sulphophenoxy)-5-pyrazolone.

Coupler 29. 1-Phenyl-3-anilino-4-(4-carboxyphenoxy)-5-pyrazolone.

Coupler 30. 1-Phenyl-3-n-pentadecyl-4-(4-hydroxyphenoxy)-5-pyrazolone.

Coupler 31. 1-Phenyl-3-{3-[α-(3-n-pentadecylphenoxy)acetamido]-benzamido}-4-(2,5-diiodo-4-hydroxyphenoxy)-5-pyrazolone.

Coupler 32. 4,4'-Bis[1-(4-cyanophenyl)-3-(5-n-butyramido-2-chloroanilino)-4-pyrazol-5-onyloxy]diphenylsulphone.

Coupler 33. 1-(4-Sulphophenyl)-3-methyl-4-(4-sulphophenoxy)-5-pyrazolone disodium salt.

Coupler 34. 1,4-Bis[1-phenyl-3-(4-n-hexanamidoanilino)-4-pyrazol-5-onyloxy]-benzene.

Coupler 35. 1-(2-Benzothiazolyl)-4-(4-nitrophenoxy)-5-pyrazolone.

Coupler 36. 1-Carbamyl-4-(4-nitrophenoxy)-5-pyrazolone.

Coupler 37. 1-Thiocarbamyl-4-(2,4-dinitrophenoxy)-5-pyrazolone.

Coupler 38. 1-Phenyl-3-phenylthio-4-(3-nitrophenoxy)-5-pyrazolone

Coupler 39. 1-Phenyl-3-methylthio-4-(3-nitrophenoxy)-5-pyrazolone

Coupler 40. 1-Phenyl-3-guanidino-4-(2,4-dinitrophenoxy)-5-pyrazolone

Coupler 41. 1-Phenyl-3-carbamyl-4-(2,4-dinitrophenoxy)-5-pyrazolone.

The colour couplers of the present invention are distinguished by their high reactivity and the very low density of unwanted colour fog they produce during colour development. The aryloxy group provides a means of attaching other substituents to the couplers such as, for example, preformed dyes useful in colour correction, dye transfer processes and the like. Additional ballasting groups can conveniently be introduced via the aryloxy group; these ballasting groups are then eliminated during the coupling reaction.

The diffusible colour couplers of the invention, such as Couplers 1, 4, 5, 27, 29 and 35 to 41 can be used in colour developer solutions used to colour develop light-sensitive elements used for colour photography which do not contain any colour coupler. Any of the well known primary aromatic amino colour-forming silver halide developing agents such as the phenylene-diamines, e.g. diethyl-*p*-phenylenediamine hydrochloride, monomethyl-*p*-phenylenediamine hydrochloride, dimethyl-*p*-phenylene-diamine hydrochloride, 2-amino-5-diethylaminotoluene hydrochloride, 2-amino-5-(N-ethyl-N-laurylamino)toluene, N-ethyl-N-(β-methanesulphonamidoethyl)-3-methyl-4-aminoaniline, or 4-[N-ethyl-N-(β-hydroxyethyl)amino]aniline, the *p*-aminophenols and their substitution products where the amino group is unsubstituted may be used in the alkaline developer solution. Various other material may be included in the developer solutions depending upon the particular requirements, for example, an alkali metal sulphite, carbonate, bisulphite, bromide or iodide and the thickening agents used in viscous developer compositions such as carboxymethyl cellulose, carboxyethyl cellulose or gelatin. The following is a typical developer solution given to illustrate but not limit the invention.

2-Amino-5-diethylaminotoluene HCl	2.0 gms.
Sodium sulphite (anhydrous)	2.0 gms.
Sodium carbonate monohydrate	20.0 gms.
Potassium bromide	1.0 gm.
Coupler	2.0 gms.
Water to	1000.0 ml.

Coupler 33 is a diffusible coupler which forms a diffusible dye on coupling development, and may be used in colour developer solutions as a competing coupler.

The other coupler examples used to illustrate the invention are nondiffusing and can be used in photographic emulsion layers. Couplers Nos. 20, 21, 22 and 28, are Fischer-type couplers. The other nondiffusing couplers, e.g., 3, 6—14, 16, 17, 23—26, 30—32, and 34, can be incorporated in emulsion layers by methods such as are described in specification No. 541,589 in which high-boiling organic solvents are used to dissolve the coupler, or by the methods described in specifications Nos. 798,512, 791,353, 791,219 or in United States Patent No. 2,949,360, in which low-boiling or water-soluble organic solvents are used with or in place of the high-boiling solvent. The use of such coupler dispersions permits thinner emulsion layers. These thinner layers are very desirable because they cause less light scattering, consequently, they produce sharper images.

The nondiffusing couplers, 2, 15, 18 and 19, contain free acid groups (i.e., carboxy and sulpho) so that the dyes formed by these couplers can be rendered diffusing. This valuable property enables these couplers to be used ot advantage in image-transfer processes and as incorporated, diffusible-dye-forming competing couplers in conventional colour films.

Coupler 22 contains a preformed dye attached to the coupler on the aryloxy group. This dye portion is split off in the areas where

the coupler combines with the oxidation products of the colour developer and diffuses out of the film. This coupler can be used as a yellow-coloured coupler so that its uncoupled residue can serve as a mask to correct for the unwanted blue absorption of magenta image dye, i.e., that formed from the coupler itself as well as that formed from other magenta couplers. Generally, such a coupler as this would be used in conjunction with another image-forming magenta coupler in the same layer.

The colour couplers of the present invention can be used in the colour development of photographic silver halide layers of the developing-out type when present in the silver halide itself or in a contiguous layer. The silver halide may be, for example, silver chloride, silver bromide, silver iodide, silver chlorobromide, silver bromoiodide or silver chlorobromoiodide. Usually the silver halide is in a hydrophilic colloid emulsion.

The hydrophilic colloid used as the vehicle for the silver halide may be, for example, gelatin, colloidal albumin, a cellulose derivative, a synthetic resin, for instance, a polyvinyl compound, or zein.

The light-sensitive layers used in conjunction with the colour couplers of the invention can be chemically or optically sensitized by any of the accepted procedures.

Usually the emulsions are coated on photographic supports in the form of multilayer colour photographic elements wherein at least three differently sensitized emulsion layers are coated over one another on the support. Usually the support is coated in succession with a red-sensitive layer, a green-sensitive layer, and a blue-sensitive layer either with or without a bleachable yellow-coloured layer, such as a Carey Lea (colloidal silver) filter layer, between the blue-sensitive and green-sensitive layers. The three differently colour sensitized layers may be arranged in any other order over one another that is desirable; however, the Carey Lea filter layer obviously would not be put over the blue-sensitive layer. Preferably, these light-sensitive layers are arranged on the same side of the support.

Elements made for image transfer processing may use a separate reception sheet which is contacted with the light-sensitive layer during its development or the reception layer may be an integral part of the light-sensitive element. Any of the support materials mentioned previously may be used for a separate reception sheet. The reception layer comprises a hydrophilic colloid layer containing a cationic mordant, e.g., the polymers of amino guanidine derivatives of vinyl methyl ketone such as described in Specification No. 850,281. Other mordants include the 2-vinyl pyridine polymer metho-*p*-toluene sulphonate and similar compounds described in specification No. 1,057,433.

The invention will be further illustrated by the following typical examples.

EXAMPLE 1.

Samples of a single layer gelatin silver bromoiodide coating were exposed (i.e., for 1/25 second on a 1B intensity scale sensitometer). These strips were then processed to colour positives by the following process; all process temperatures were 68°.

MQ Developer	5 minutes
"Kodak F—5 Fixing Bath	5 minutes
Reexposure (i.e., 12" 100 watt bulb)	1 minute
Colour Developer (formula below)	10 minutes
"Kodak" F—5 fixing Bath	5 minutes
Water wash	5 minutes
Bleach (ferricyanide)	5 minutes
Water Wash	5 minutes
"Kodak" F—5 Fixing Bath	5 minutes
Water Wash	10 minutes
Dry	

("Kodak" is a Registered Trade Mark)

Developer Formula:

Benzyl alcohol	4 ml.
Sodium hexametaphosphate	0.5 gms.
Sodium sulphite desicated	2.0 gms.
Sodium hydroxide	0.16 gms.
Coupler*	2.0 gms.
4-Amino-3-methyl-N-ethyl-N-β-(methanesulphanamido)-ethyl-aniline sesquisulphate hydrate	5.0 gms.
Sodium carbonate monohydrate	50.0 gms.
Sodium bromide	0.2 gms.
Water to pH to 10.75	1 litre

* The colour couplers used in the above-mentioned developer formula were Nos. 1, 4, 5, 27 and 29, respectively.

Good magenta dye images were formed in each of the respective strips.

EXAMPLE 2.

Single layer gelatin silver bromoiodide coatings were prepared containing Colour Couplers Nos. 3, 6, 8, 11, 13, 17, 23 and 24, respectively. Each of these colour couplers was dispersed in said coating in the form of a finely-dispersed solution of the colour coupler in coupler solvent, di-n-butylphthalate. These coatings contained 10 parts of gelatin, 5 parts of silver, 2 parts of colour coupler, and 1 part of coupler solvent. Samples of the above-mentioned coatings were given 1/25 second exposure on a 1B intensity scale and processed in a conventional manner to colour negatives, respectively, using the following developer solution.

Sodium sulphite (anhydrous)	2.0 gms.
2-Amino-5-diethylaminotoluene HCl	2.0 gms.
Sodium carbonate monohydrate	20.0 gms.
Potassium bromide	2.0 gms.
Water to pH to 10.86	1.0 litre

Each of the processed strips contained high quality magenta dye images.

EXAMPLE 3.

Single layer gelatin silver bromoiodide coatings containing Colour Couplers Nos. 2, 15, 18 and 19, respectively, were prepared. These coatings were similar to those described in Example 2 above except that the colour couplers were dispersed directly in the gelatin. Samples of these coatings were exposed as described in Example 2 above, and processed by developing each of them for 5 minutes at 75°F in contact with a receiving sheet containing a mordant which had been presoaked in the following developer solution.

Sodium carbonate monohydrate	22.0 gms.
Ascorbic acid	0.24 gms.
Potassium bromide	0.8 gms.
Sodium sulphite (anhydrous)	2.0 gms.
4-Amino-N-ethyl-N-β-hydroxyethyl-aniline sulphate	11.0 gms.
Water to make pH adjusted to 12.5 using 20% sodium hydroxide solution.	1.0 litre

After the development period, samples of the film were removed from the mordant receiving sheet, in which sheets were contained the respective transferred and mordanted magenta dye images.

Similarly, other colour couplers of the invention can be used in colour photography as illustrated previously with representative couplers. Further, the colour couplers of the invention are valuable as magenta image-forming couplers in multilayer photographic colour films containing other classes of colour couplers in the other layers of said film. Such other colour couplers are, for example, yellow image-forming couplers containing a methylene or substituted methylene group having two

carbonyl groups directly attached thereto, and cyan-forming couplers such as naphthols and phenols.

In general, the colour couplers of the present invention can be prepared by the reaction of an ethyl α-aryloxyacylacetate or an ethyl α - aryloxy - β - methylthio - β-anilinoacrylate (including substituted aryloxy compounds) with an aromatic hydrazine. The intermediate ester is prepared by reacting an aromatic hydroxy compound with an ethyl α-halo-β-ketoester in the presence of an alkaline condensing agent. The colour couplers of the invention in which R^3 represents an acylamino group can be made by the reaction of a diethyl α-aryloxyoxaloacetate, followed by hydrolysis of the resulting 3-carbethoxypyrazolone, conversion of the resulting free acid to the acid azide, heating in a solvent to effect Curtius rearrangement to the 3-aminopyrazolone and acylation of this with the appropriate acid chloride.

Alternatively, the colour couplers of the invention can be prepared by reacting the sodium salt of 4-hydroxy-5-pyrazolone with a fluoro benzene compound, which fluoro benzene compound is activated by having an electron withdrawing substituent or substituents attached to the benzene ring, e.g., a nitro or sulpho group or groups, or further fluorine atoms.

The following preparations will illustrate the various methods which were used to prepare the magenta-forming colour couplers of the invention.

Preparation of Coupler 1.

1-phenyl-3-methyl-4-(4-methylsulphonylphenoxy)-5-pyrazolone:

The intermediate ethyl 2 - (4 - methylsulphonylphenoxy) - acetoacetate was prepared as follows. To a hot solution of 17 gms. of 4-methylsulphonylphenol and 10 gms. of triethylamine in 250 ml. of acetonitrile was added 16 gms. of ethyl-2-chloroacetoacetate. The reaction mixture was refluxed for six and a half hours, after which time it was left overnight at room temperature. The triethylamine hydrochloride which precipitated from the mixture was separated and the resultant solution was concentrated to a volume of 25 ml. Additional triethylamine hydrochloride which separated was again removed. To the concentrated solution was then added 300 ml. of cold water, whereupon a white solid precipitated, was collected and air dried. This solid was recrystallized once from a mixture of 150 ml. of ethyl alcohol and 300 ml. of water, and a second time from 100 ml. of methyl alcohol to yield 8.5 gms. of product having a melting point of 108—109°C.

A mixture of 2 gms. of ethyl 2 - (4 - methylsulphonylphenoxy) - acetoacetate (prepared as above) and 1 gm. of phenylhydrazine hydrochloride in 25 ml. of absolute ethyl alcohol was refluxed for 1 hour. The resulting clear solution was allowed to cool to room temperature, whereupon a solid separated. This solid was recrystallized from 100 ml. of ethyl alcohol to yield the product, Coupler 1.

Preparation of Coupler 2.

1-(4-sulphophenyl)-3-methyl-4-[4-(N-methyl-N-n-octadecylsulphamyl)phenoxy]-5-pyrazolone sodium salt:

A mixture of 5.7 gms. of ethyl α - acetyl-α - [4 - (N - methyl - N - n - octadecylsulphamyl)phenoxy]acetate, 1.9 gms. of *p*-hydrazinobenzene sulphonic acid, and 0.82 gms. of sodium acetate in 50 ml. of glacial acetic acid was refluxed for 1 hour, after which time an additional 0.82 gms. of sodium acetate was added to the hot solution. The reaction mixture was refluxed for an additional 30 minutes and allowed to cool to room temperature overnight, during which time a solid separated. This solid was collected and air dried. To the filtrate was added 150 ml. of ethyl ether, and the solid which separated was also collected. The total solids were combined and recrystallized from 20 ml. of dimethylformamide to yield the product, Coupler 2.

Preparation of Coupler 3.

1-(2,4,6-trichlorophenyl)-3-{3-[α-(2,4-di-t-amylphenoxy)acetamido]benzamido}-4-(4-nitrophenoxy)-5-pyrazolone:

Intermediate No. 1. 1 - (2,4,6 - Trichlorophenyl) - 3 - {3 - [α - 2,4 - di - t - amylphenoxy)acetamido]benzamido} - 4 - hydroxyimino - 5 - pyrazolone: To a solution of 67 gms. of 1 - (2,4,6 - trichlorophenyl) - 3 - {3-[α - (2,4 - di - t amylphenoxy)acetamido]benzamido} - 5 - pyrazolone in 500 ml. of glacial acetic acid was added 12 gms. of isopentyl nitrite with stirring at room temperature. The reaction mixture was stirred for approximately 20 minutes, after which time an orange solid began to precipitate. The mixture was stirred for a total of 1 hour, and the solid which separated was collected and recrystallized from ethyl alcohol to yield 56 gms. of the product, m.p. 145—148°C.

Intermediate No. 2. 1 - (2,4,6 - trichlorophenyl) - 3 - {3 - [α - (2,4 - di - t - amylphenoxy)acetamido]benzamido} - 4 - amino-5 - pyrazolone tin ($SnCl_4$) salt: To a solution of 5 gms. of Intermediate No. 1 above in 150 ml. of ethyl alcohol (denatured with 5% of methyl alcohol) was added a mixture of 7 gms. of anhydrous stannous chloride in 20 ml. of concentrated hydrochloric acid. The resultant solution was warmed on a steam bath for 10 minutes, during which time it changed from a bright orange colour to a very pale yellow. The mixture was cooled to room temperature and poured into 200 ml. of cold water, whereupon a white solid separated, was collected and air dried to yield the product.

Intermediate No. 3. 1 - (2,4,6 - trichlorophenyl) - 3 - {3 - [α - (2,4 - di - t - amylphenoxy)acetamido]benzamido} - 4,4 - dihydroxy - 5 - pyrazolone: To a solution of 2.5 gms. of Intermediate 2 above in 25 ml. of ethyl alcohol was added a hot solution of 20 gms. of ferric chloride hexahydrate ($FeCl_3 . 6H_2O$) and 5 ml. of concentrated hydrochloric acid in 100 ml of ethyl alcohol (denatured with 5% of methyl alcohol). The resultant solution was heated on a steam bath for 10 minutes, after which time it was cooled to room temperature and poured into 200 ml. of cold water, whereupon a white solid separated, was collected and dried to yield 1.8 gms. of the product.

Intermediate No. 4. 1 - (2,4,6 - trichlorophenyl) - 3 - {3 - [α - (2,4 - di - t - amylphenoxy)acetamido]benzamido} - 4 - hydroxy-5 - pyrazolone: A solution of 1.2 gms. of Intermediate No. 3 above in 50 ml. of absolute ethyl alcohol was hydrogenated on the low pressure Parr hydrogenation apparatus using 10% palladium on charcoal as the catalyst for 20 minutes at room temperature. The reduction solution was then filtered to remove the catalyst, concentrated in vacuo to yield the product, which was used without further purification.

Coupler 3, named above: To a solution of Intermediate No. 4 above and an equivalent amount of anhydrous sodium methylate in 10 ml. of dimethyl formamide (i.e., which had been saturated with nitrogen) was added an equivalent amount of 4-nitrofluorobenzene. The resultant solution was heated on a steam bath for two and a half hours, after which time was added 10 ml. of 5% acetic acid, whereupon a solid precipitated, was collected, and recrystallized from methyl alcohol to yield the product.

Preparation of Coupler 4.

1-Phenyl-3-methyl-4-(2,4-dinitrophenoxy)-5-pyrazolone.

To a solution of 1 gm. of 1-phenyl-3-methyl-4-hydroxy-5-pyrazolone and 0.5 gm. of sodium methylate in 5 ml. of dimethyl formamide (which had been saturated with nitrogen) was added 1 gm. of 2,4-dinotrofluorobenzene with stirring at room temperature. The reaction mixture was stirred at room temperature for 30 minutes (cooling in an ice bath was required), after which time the solution was acidified with dilute acetic acid, whereupon a solid precipitated, was collected and dried to yield the product.

Preparation of Coupler 5.

1-Phenyl-3-anilino-4-phenoxy-5-pyrazolone.

Intermediate No. 1. Ethyl α-phenoxyacetoacetate: To a slurry of 23 gms. of sodium phenolate in 1 litre of dry anhydrous benzene heated to reflux was added 165 gms. of ethyl α-chloroacetoacetate with stirring over a period of 30 minutes. The reaction mixture was stirred and refluxed for 4 hours, after which time it was washed with 2×500 ml. of water, dried over magnesium sulphate, filtered, and concentrated in vacuo to yield the product.

Intermediate No. 2. Ethyl α - phenoxy-α - isothiocyano - acetoacetate sodium salt: To a refluxing solution of sodium etholate (i.e., prepared by reacting 23 gms. of metallic sodium in 300 ml. of methanol) in 300 ml. of absolute ethyl alcohol was added Intermediate No. 1 above. To the resultant solution was then added 135 gms. of phenylisothiocyanate over a period of 5 minutes with stirring. This solution was refluxed for an additional 5 minutes after the addition had been completed, after which time it was cooled to 20°C. The product was isolated and used as such.

Intermediate No. 3. Ethyl α - phenoxy - β-methylthio - β - anilinoacrylate: To a solution of Intermediate No. 2 above was added, at room temperature with stirring, 147 gms. of iodomethane. The solution was allowed to stir at room temperature for 15 minutes and then was refluxed for an additional 15 minutes. The product was isolated and used as such.

Coupler 5, named above: To the refluxing solution of Intermediate No. 3 above was added 108 gms. of phenylhydrazine. The resultant solution was refluxed for 6 hours, after which time it was cooled to room temperature, and held at room temperature for 2 days. A small amount of solid which had separated was filtered off and the filtrate was mixed with 1 litre of diethyl ether. The whole was then extracted with 3×500 ml. of water, dried over magnesium sulphate, filtered and concentrated in vacuo, and purified (i.e., by electrophoresis) to yield the product, Coupler 5.

Couplers 6, 8, 10, 11, 15, 19, 20, 22, 25, 28, 29 and 33 were each prepared in accordance with the procedure used to prepare Coupler 3 using the respective intermediates given in the following Table A.

TABLE A

Coupler No.	Coupler Intermediate	Fluorobenzene
6	1-Phenyl-3-n-octadecylamino-4-hydroxy-5-pyrazolone	4-Nitrofluorobenzene
8	1-{4-[α-(3-n-Pentadecylphenoxy)-n-butyramido]phenyl}-3-ethoxy-4-, hydroxy-5-pyrazolone	4-Nitrofluorobenzene
10	1-(4-Stearamidophenyl)-3-ethoxy-4-ethoxy-4-hydroxy-5-pyrazolone	2,4-Dinitrofluoro-benzene
11	1-[4-(4-t-Butylphenoxy)phenyl]-3-[α-(4-t-butylphenoxy)-n-propionamido]-4-hydroxy-5-pyrazolone	Hexafluorobenzene
15	1-Methyl-3-(3,5-dicarbomethoxy-benzamido)-4-hydroxy-5-pyrazolone (The ester was then hydrolysed to the free acid, Cplr. 15, using alkaline hydrolysis).	4-Nitro-3-penta-decylfluorobenzene
19	1-Phenyl-3-[N'-(β,{-dicarbethoxy-ethyl)ureido]-4-hydroxy-5-pyra-zolone (The ester was then hydro-lyzed to the free acid, Cplr. 19, using alkaline hydrolysis).	4-Nitro-3-penta-decylfluorobenzene
20	1-(2,4-Dichloro-6-methoxyphenyl)-3-{3-[α-(3-n-pentadecyl-4-sulpho-phenoxy)acetamido]-benzamido}-4-hydroxy-5-pyrazolone	4-Nitrofluoro-benzene
25	1-(2,4,6-Trichlorophenyl)-3-{2-[α-(3-n-pentadecylphenoxy)acetamido]-anilino}-4-hydroxy-5-pyrazolone	4-Nitrofluoro-benzene
28	1-(2,4,6-Trichlorophenyl)-3-{2-chloro-4-[α-(2,4-di-t-amyl-phenoxy)-n-butyramido]anilino}-4-hydroxy-5-pyrazolone	4-Fluorobenzene sulphonic acid
29	1-Phenyl-3-anilino-4-hydroxy-5-pyrazolone	4-Fluorobenzoic acid
33	1-(4-Sulphophenyl)-3-methyl-4-hydroxy-5-pyrazolone (The free acid was converted to the di-sodium salt with sodium acetate).	4-Fluorobenzene sulphonic acid
22	1-Phenyl-3-{2-chloro-4-{3-[α(3-penta-decylphenoxy)acetamido]-benz-amido}-anilino}-4-hydroxy-5-pyrazolone	4-(4-Fluorophenyl-azo)benzene sul-phonic acid

Couplers 35 to 41 can be prepared by the procedure used to prepare Coupler 3 using the respective intermediates given in the following Table A'.

TABLE A'

Coupler No.	Coupler Intermediate	Fluorobenzene
35	1-(2-Benzothiazolyl)-4-hydroxy-5-pyrazolone	4-Nitrofluorobenzene benzene
36	1-Carbamyl-4-hydroxy-5-pyrazolone	4-nitrofluorobenzene
37	1-Thiocarbamyl-4-hydroxy-5-pyrazolone	2,4-dinitrofluoro-benzene
38	1-Phenyl-3-phenylthio-4-hydroxy-5-pyrazolone	3-nitrofluorobenzene
39	1-Phenyl-3-methylthio-4-hydroxy-5-pyrazolone	3-nitrofluorobenzene
40	1-Phenyl-3-guanidino-4-hydroxy-5-pyrazolone	2,4-dinitrofluoro-benzene
41	1-Phenyl-3-carbamyl-4-hydroxy-5-pyrazolone	2,4-dinitrofluoro-benzene

Couplers 7, 21 and 26 were each prepared by the catalytic reduction (i.e., using palladium on charcoal as the catalyst) of Couplers 6, 20 and 25, respectively. The amino intermediates formed were then each acylated using acetyl chloride to yield Couplers 7, 21 and 26, respectively.

Couplers 9, 12, 13, 14, 16, 17, 30 and 31 were each prepared in accordance with the procedure given for Coupler 1; Couplers 18, 23, 24 and 27 were each prepared in accordance with the procedure given for Coupler 5 using the respective intermediates given in Table B below.

TABLE B

Coupler No.	Ester Intermediate	Hydrazine Intermediate
9	Ethyl 2-[2-chloro-4-sulphonamido]-phenoxy-3-oxo-n-octadecanoate	Phenylhydrazine
12	Diethyl-α-[1-naphthyloxy]oxaloacetate (Ring closed to the 3-carbethoxypyrazolone; hydrolyzed to the acid; converted to the acid azide; Curtius rearrangement to the 3-amino-pyrazolone; acrylate the amine with the appropriate acid chloride, 4-t-butylphenoxy-α-methylacetyl chloride).	4-(4-t-Butylphenoxy)-phenylhydrazine
13	Diethyl-α-[4-pyridyloxy]oxaloacetate (Ring closed to the 3-carbethoxypyrazolone; then as in No. 12).	4-(4-t-Butylphenoxy)-phenylhydrazine
14	Diethyl-α-[4-chloro]phenoxyoxaloacetate (Ring closed to 3-carbethoxypyrazolone; then as in No. 12).	4-(4-t-Butylphenoxy)-phenylhydrazine
16	Diethyl-α-[4-N-methyl-N-phenylsulphonamido]-phenoxyoxaloacetate (Ring closed to 3-carbethoxypyrazolone; then as in No. 12).	Phenylhydrazine

No. Coupler	Coupler Intermediate	Fluorobenzene
17	Diethyl-α-[4-(4-hydroxyphenyl)sulphonyl-phenoxy]oxaloacetate (Treated as in No. 12).	2,4,6-Trichlorophenyl-hydrazine
18	Ethyl-α-[4-octadecyloxy]-phenoxy-β-methyl-thio-β-[3,5-dicarboxy]anilinoacrylate	Phenylhydrazine
23	Ethyl-α-[4-N,N-diethylsulphamyl]phenoxy-β-methylthio-β-[2-methoxy-5-nitro]-anilino-acrylate (Ring closure followed by hydro-genation of nitro function to amino; acrylate amine with appropriate acid chloride, 2,4-di-t-amylphenoxyacetyl chloride).	2,4,6-Trichloro-phenylhydrazine
24	Ethyl-α-[4-methylsulphonyl]-phenoxy-β-methylthio-β-2,4-dichloroanilinoacrylate	2,6-Dichloro-4-nitro-phenylhydrazine. The intermediate Nitro com-pound was catalytically reduced and the resultant amino compound was acylated with α-(4-t-butylphenoxy)-n-tetra-tetra decanoyl chloride to yield Coupler 24
27	Ethyl-α-[4-sulphamyl]phenoxy-β-methylthio-β-4-nitroanilinoacrylate	2,4,6-Trich.loro-phenylhydrazine
30	Ethyl-2-[4-hydroxy]phenoxy-3-oxooctadecanoate	Phenylhydrazine
31	Diethyl-α-[2,5-diiodo-4-hydroxy]phenoxy-oxaloacetate (Ring closed to the 3-carbethoxy-pyrazolone, hydrolyzed to the acid; converted to acid chloride; converted to acid azide; Curtius rearrangement to the 3-aminopyra-zolone; 3-amino function acylated with the appropriate acid chloride, 3-[α-(3-n-pentadecyl-phenoxy)-acetamido]benzoyl chloride).	Phenylhydrazine
32	4,4'-Sulphonyldiphenol bis[α-carbethoxy-β-methylthio-β-(2-chloro-5-nitro)anilino-vinyl ether] (Chemically reduce the nitro function to amine and acylate amine with n-butyryl chloride).	4-Cyanophenyl-hydrazine
34	Hydroquinone bis[α-carbethoxy-β-methylthio-β-*p*-nitroanilino vinyl ether] (Catalytically hydrogenate the nitro function to amine and acylate amine with n-hexanoyl chloride).	Phenylhydrazine

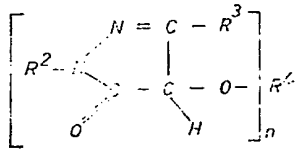
The colour couplers of the present invention produce little or no colour fog, have very good coupling reactivity, and exhibit very low printout and yellowing when they are incorporated into photographic coatings relative to that exhibited by many of the known magenta couplers. Printout is the percent change in transmission (i.e., to a light source having a predominant wavelength of 420 mμ) that is produced in an area of the processed strip having no exposure (i.e., D min area) by 30 hours' exposure to a Xenon arc lamp. Yellowing is the percent change in transmission (i.e. to a light source having a predominant wavelength of 420 mμ) produced in an unexposed area of the processed strip (i.e.,

D min area) by exposing the strip for 1 week to a temperature of 140°F and 40% relative humidity.

WHAT WE CLAIM IS:—

1. A colour coupler containing at least one 4-pyrazolyl-5-one group having attached to the carbon atom in the 4-position, a hydrogen atom and an aryloxy or substituted aryloxy group.

2. A colour coupler of the general formula:

(III) 

wherein n represents 1 or 2,

R^2 represents an alkyl group, a monocyclic alkyl group, a bicyclic alkyl group, a substituted alkyl group, an aryl or substituted aryl group, a heterocyclic (substituted or unsubstituted) group, a carbamyl group or a thiocarbamyl group,

R^3 represents a hydrogen atom, an alkyl or substituted alkyl group, an aryl or substituted aryl group, a heterocyclic group (substituted or unsubstituted), a carboxy ester group, an etherified hydroxyl group, an etherified thiol group, an amino or substituted amino group, an acylamino group, a carbamyl group, a sulphamyl group, a ureido group, a thioureido group or a guanidino group, and

R^4 represents an aryl or substituted aryl group when n represents 1, or an arylene or substituted arylene group when n represents 2.

3. The colour coupler 1 - phenyl - 3-methyl - 4 - (4 - methylsulphonylphenoxy) - 5-pyrazolone.

4. The colour coupler 1 - (4 - sulphophenyl) - 3 - methyl - 4 - [4 - (N - methyl-N - octadecylsulphamyl)phenoxy] - 5 - pyrazolone sodium salt.

5. The colour coupler 1 - (2,4,6 - trichlorophenyl) - 3 - {3 - [α - (2,4 - di - t-amylphenoxy)acetamido]benzamido} - 4 - (4-nitrophenoxy) - 5 - pyrazolone.

6. The colour coupler 1 - phenyl - 3-methyl - 4 - (2,4 - dinitrophenoxy) - 5 - pyrazolone.

7. The coupler 1 phenyl - 3 - anilino-4 - phenoxy - 5 - pyrazolone.

8. The colour coupler 1 - {4 - [α - (3-pentadecylphenoxy) - butyramido]phenyl} - 3-ethoxy - 4 - (4 - nitrophenoxy) - 5 - pyrazolone.

9. The colour coupler 1 - [4 - (4 - t-butylphenoxy)phenyl] - 3 - [α - (4 - t - butylphenoxy)propionamido] - 4 - (4 - chlorophenoxy) - 5 - pyrazolone.

10. The colour coupler 1 - (2,4 - dichloro - 6 - methoxyphenyl) - 3 - {3 - [α-(3 - pentadecyl - 4 - sulphophenoxy)acetamido]benzamido} - 4 - (4 - nitrophenoxy)-5 - pyrazolone.

11. An image-forming layer containing a colour coupler which is as claimed in any of claims 1 to 10.

12. A light-sensitive hydrophilic colloid silver halide emulsion containing a colour coupler which is as claimed in claim 1 or 2.

13. A light-sensitive hydrophilic colloid silver halide emulsion containing a colour coupler which is as claimed in any of claims 3 to 10.

14. A photographic emulsion as claimed in claim 13 in which the hydrophilic colloid is gelatin.

15. A colour developer containing a primary aromatic amino developing agent and a diffusible colour coupler which is as claimed in claim 1.

16. A colour developer containing a primary aromatic amino developing agent and a diffusible colour coupler which is as claimed in claim 2.

17. A photographic element comprising a support bearing at least one layer of or containing a photographic emulsion as claimed in claim 12, 13 or 14.

18. A process of colour development which includes developing a reducible silver salt image with an aqueous developer solution comprising an alkali and a primary aromatic amino developing agent in the presence of a colour coupler which is a compound as claimed in any of claims 1 to 10.

19. The processes of colour development employing the 2-equivalent magenta-forming colour couplers claimed in claim 1 or 2 and as herein particularly described.

20. The hydrophilic colloid-silver halide light-sensitive emulsions containing the 2-equivalent magenta-forming colour couplers claimed in claim 1 or 2 and as herein particularly described.

21. The 2-equivalent colour couplers claimed in claim 2 and as herein particularly described, other than those claimed in claims 3 to 10.

W. P. THOMPSON & CO.,
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Fig.1.

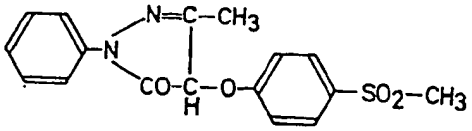


Fig.2.

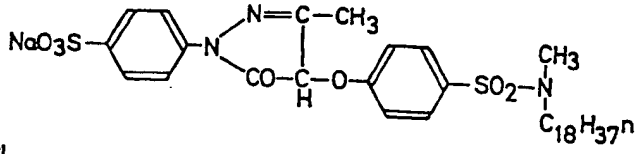


Fig.3.

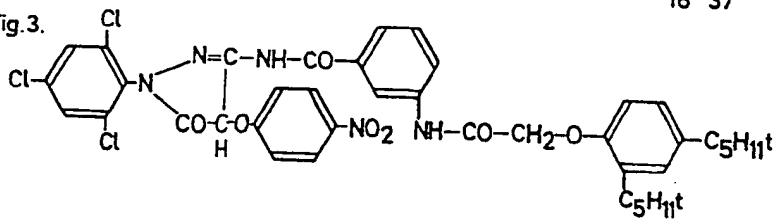


Fig.4.

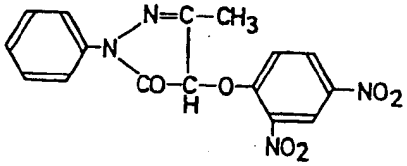


Fig.5.

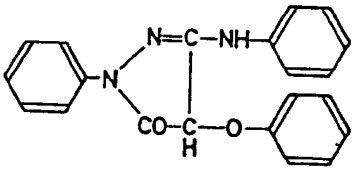


Fig.6.

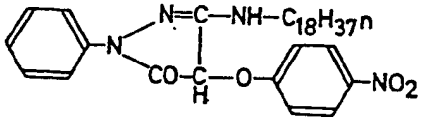
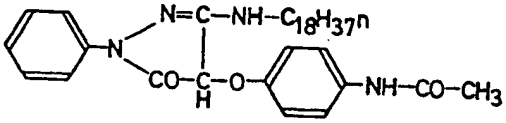


Fig.7.



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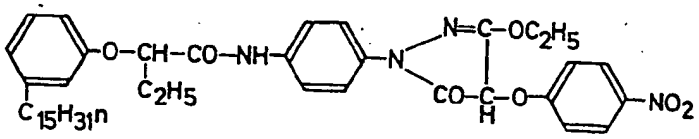
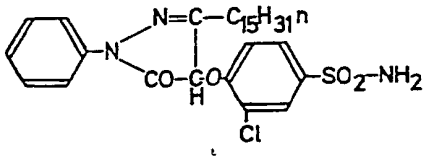


1140898 COMPLETE SPECIFICATION

8 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheets 1 & 2

Fig.9.



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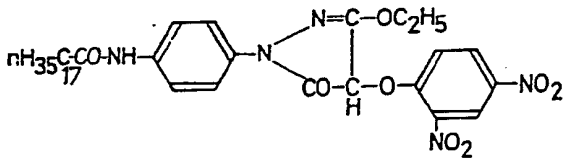

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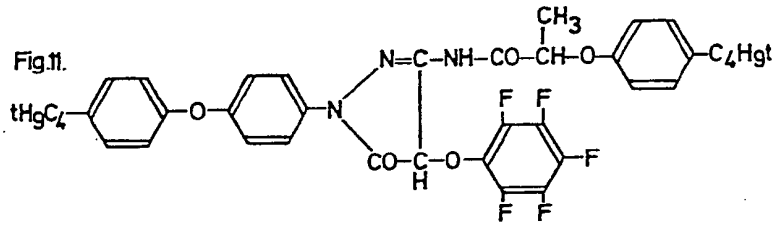

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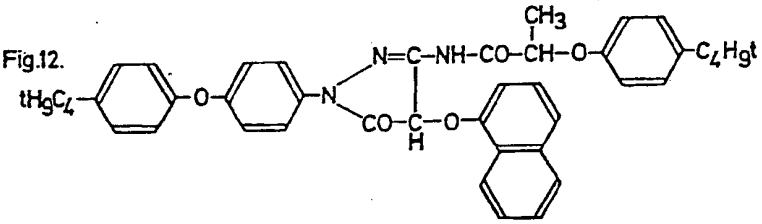

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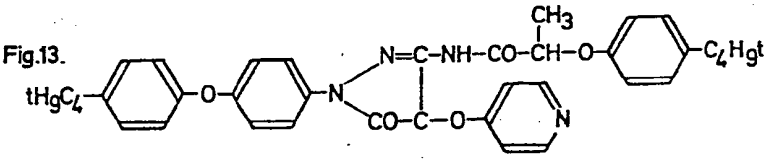

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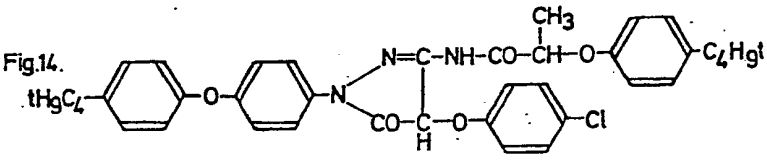

8 SHEETS

This drawing is a reproduction of the Original on a reduced scale

Sheets 1 & 2

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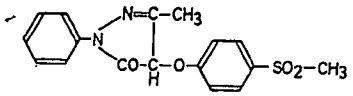

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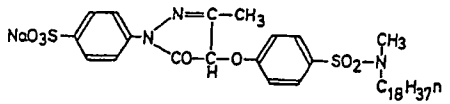

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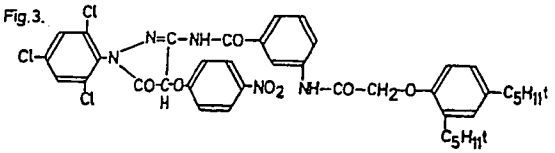

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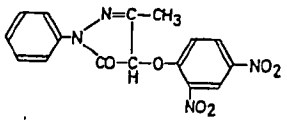

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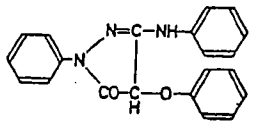

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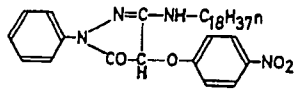

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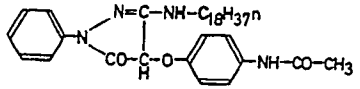

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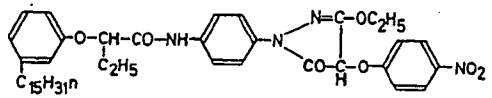

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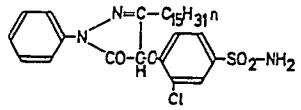

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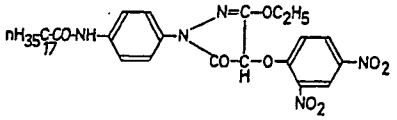

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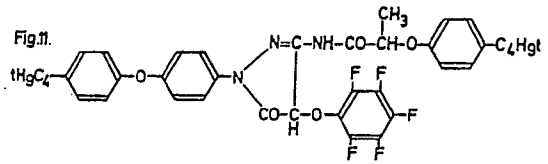

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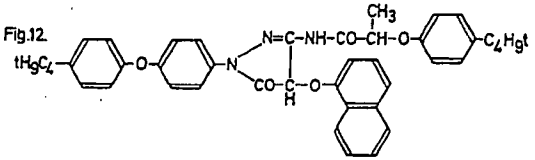

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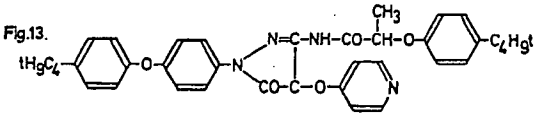

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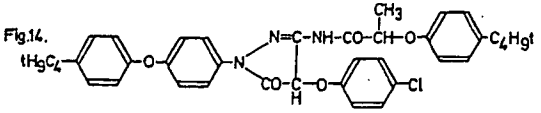

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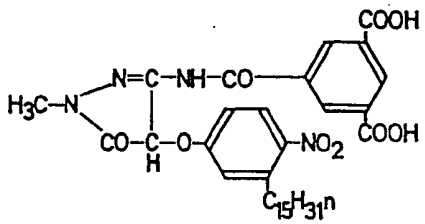

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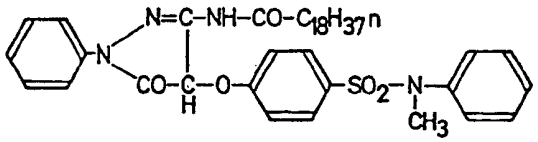

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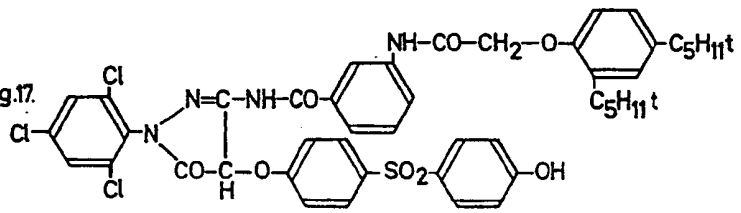

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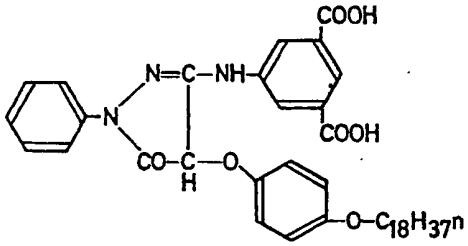

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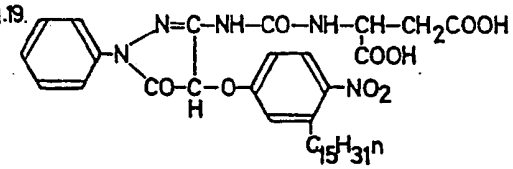
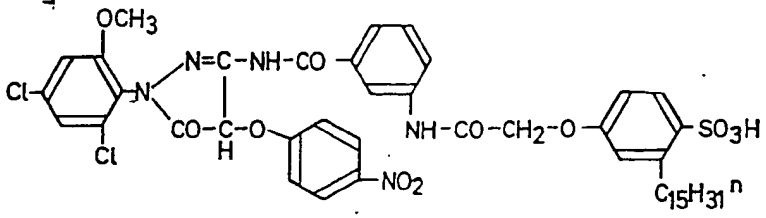


1140898 COMPLETE SPECIFICATION
8 SHEETS *This drawing is a reproduction of the Original on a reduced scale*
Sheets 3 & 4

Fig.20.



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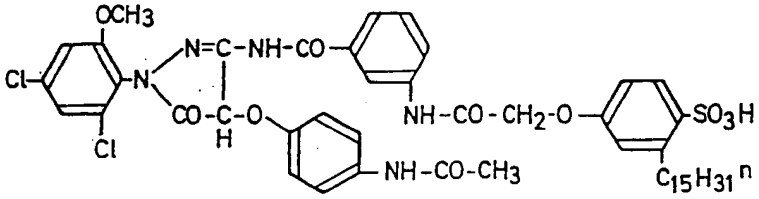

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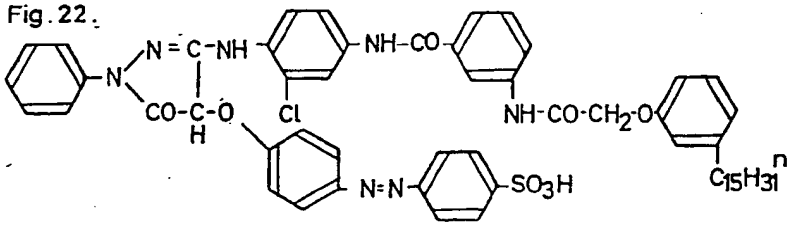

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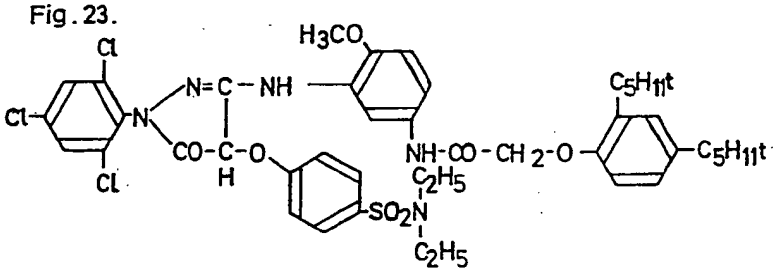

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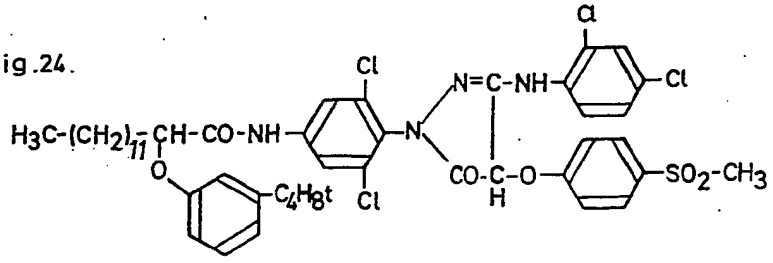

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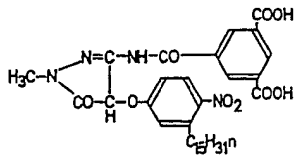

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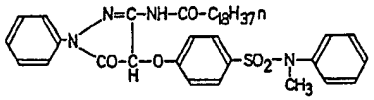

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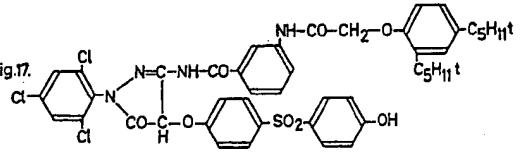

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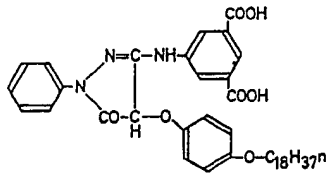

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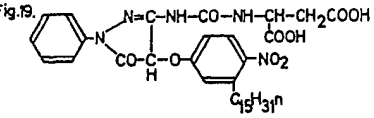

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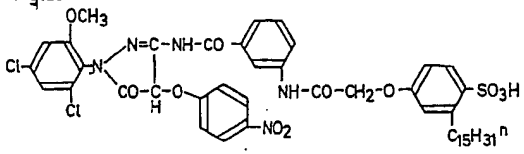

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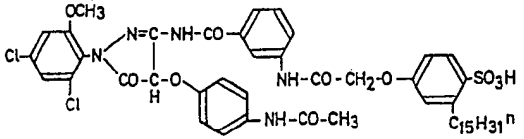

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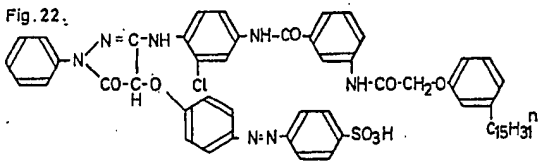

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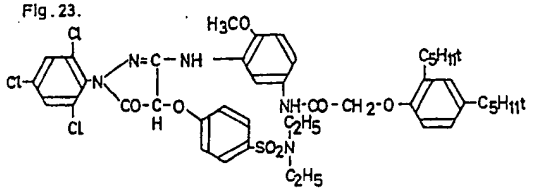

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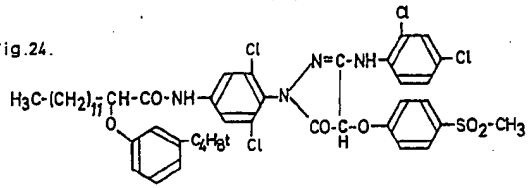

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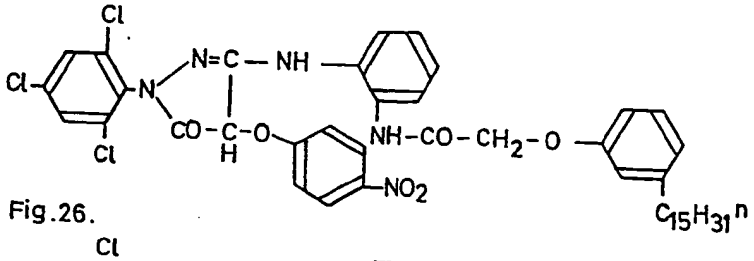

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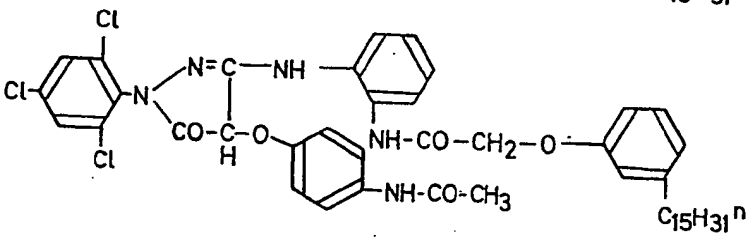

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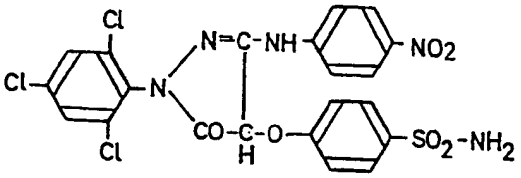

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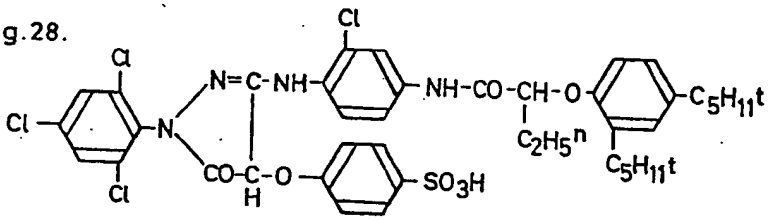

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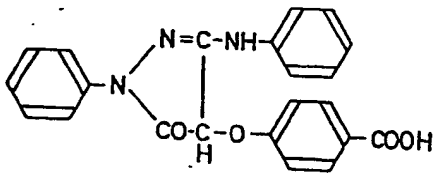
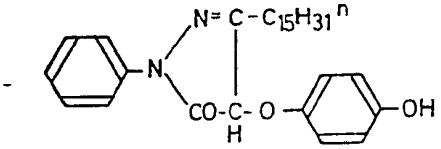


1140898 COMPLETE SPECIFICATION
8 SHEETS *This drawing is a reproduction of the Original on a reduced scale*
Sheets 5 & 6



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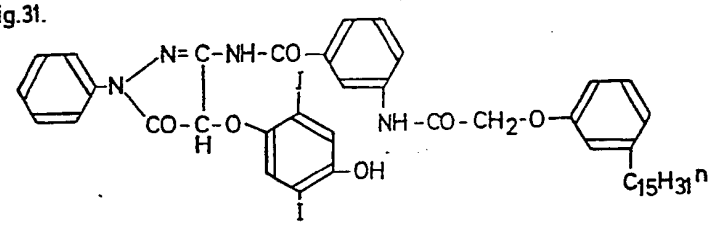

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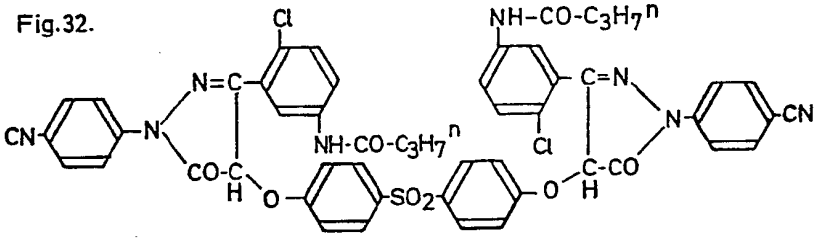


Fig.33

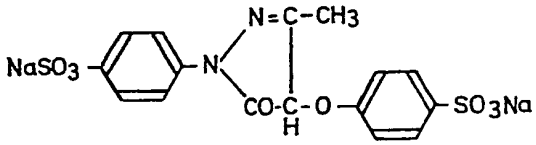
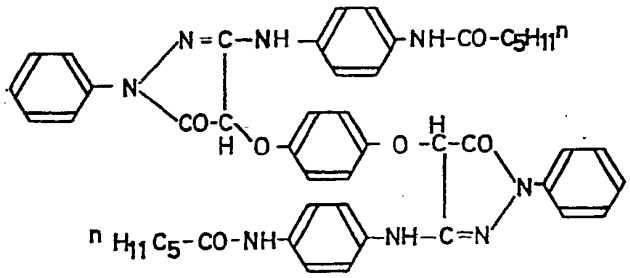


Fig.34.



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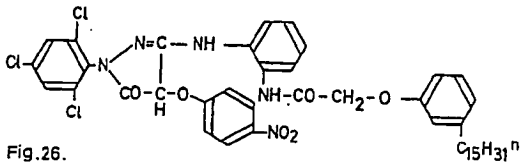

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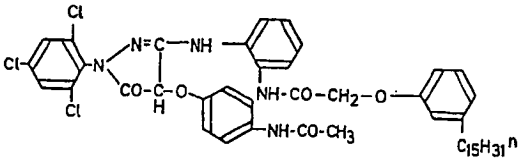

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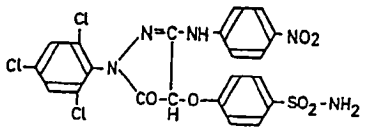

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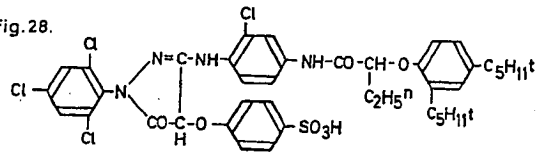

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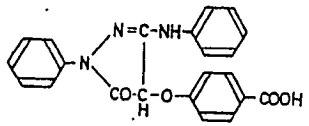

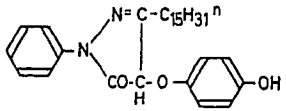

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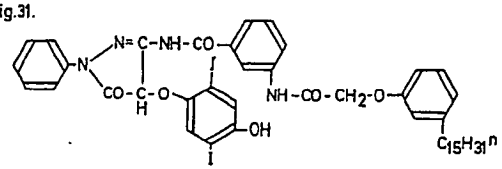

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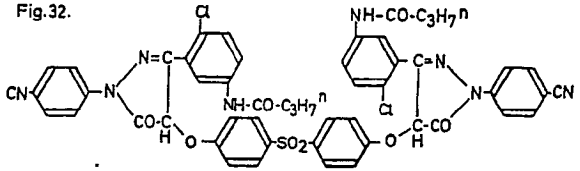

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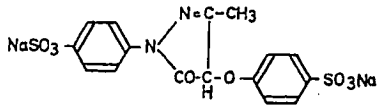

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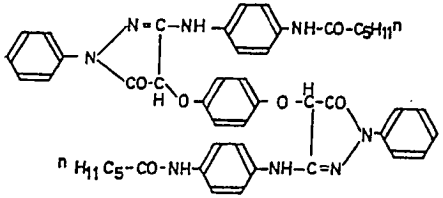

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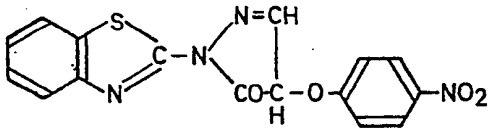

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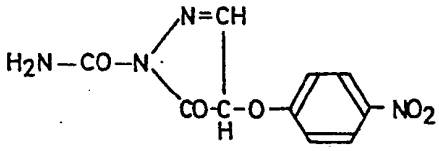

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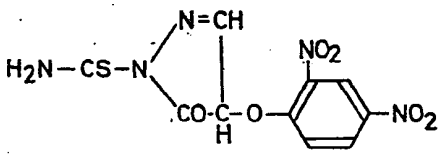

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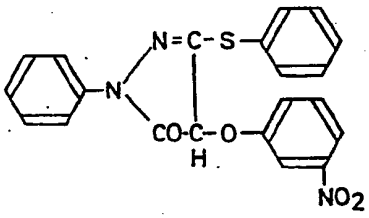

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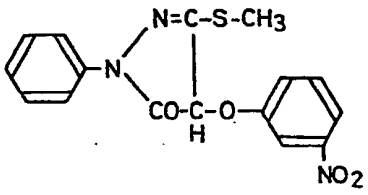

1140898 COMPLETE SPECIFICATION

8 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

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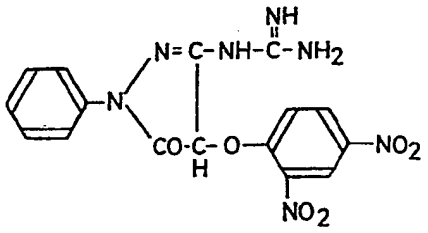

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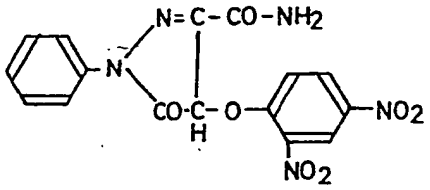

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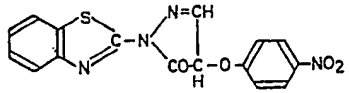

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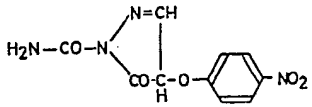

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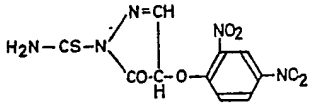

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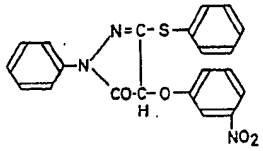

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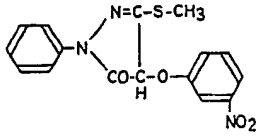

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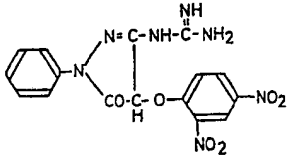

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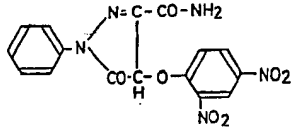

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Patent Abstracts of Japan

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APPLICANT : MITSUBISHI CHEM IND LTD;

INVENTOR : SAKURAI YOKO;

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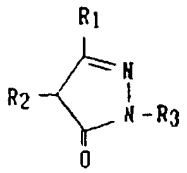
TITLE : PEROXIDIZED LIPID-FORMATION INHIBITOR



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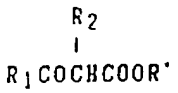

II

III

ABSTRACT : PURPOSE: The titled preparation that contains, as an active ingredient, a pyrazolone derivative or its salt, thus being used as a good preventive or remedy for a variety of ischemic diseases or other diseases caused by them, e.g., cerebral infarction or hemorrhage and other cerebrovascular diseases or cerebral hy pofunction caused by them.

CONSTITUTION: The objective preparation contains, as an active ingredient, a pyrazolone derivative of formula I (R_1 is H, aryl, 1~5C alkyl, 3~6C alkoxycarbonylalkyl; R_2 is H, aryloxy, arylmercapto, 1~5C alkyl; or R_1 and R_2 incorporate to form 3~5C alkylene; R_3 is residue of heterocyclic ring) or its pharmaceutically permissible salt. It is applied orally, intravenously or rectally. The active ingredient of formula I is synthesized by reaction of a β-ketoacid derivative of formula II (R' is 1~5C alkyl) with a hydrazine derivative of formula III.